Argonne National Laboratory

SOME METALLURGICAL APPLICATIONS OF AUTORADIOGRAPHY

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Chemical Engineering Division

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ABSTRACT

Macro- and high-resolution methods for autoradiography were used to investigate a number of problems concerning the distribution of uranium and other active elements in metal specimens. Illustrations are presented of the behavior of some of these materials with various heating and cooling treatments and in the presence of metals with which intermetallic phases are formed. Techniques are discussed for handling and examining autoradiographic stripping films by means of various types of metallurgical and conventional microscopic equipment.

I. INTRODUCTION

In 1896 Henri Becquerel simultaneously discovered natural radioactivity and autoradiography.[1] In the years that followed, autoradiography was largely superseded by other more quantitative and sensitive techniques for the detection and measurement of radioactivity, although it continued to find occasional use for certain specialized applications, mainly in biological work. Within the past fifteen years, however, it has received a new impetus, largely as a result of improvements in radiation-sensitive emulsions and techniques, particularly in high-resolution work.

Autoradiography is not generally considered to be a quantitative technique. With proper standardization[2] of exposures and reference samples, however, it can give highly accurate evaluations of activity. Generally it is used as a qualitative technique. No other method can give as graphic and complete a description of the distribution of activity within a specimen. With the high-resolution techniques currently available, it becomes possible to determine precisely the locations of disintegrating particles by observing individual tracks in the emulsion.

Although autoradiographic techniques have been used most often for the determination of activity in biological specimens, they can also be of great value in chemical and metallurgical work.[3] Several applications to pyrometallurgical and other process development work are described in

this report. No attempt is made to discuss the general principles of autoradiography, since this subject has been covered in excellent review articles by Norris[4] and others.

The distribution of one metal in another is often difficult to determine by means of ordinary analytical methods. If the concentration of one component is small, large samples are usually required for chemical analysis, and the results are of dubious value in distinguishing local variations in composition. Metallographic methods are often uninformative in the case of very dilute alloys. Analyses of these alloys become simpler when radioactive tracers for the minor constituent are available. Radioactive counting is a sensitive and accurate method of analysis, but the results are still subject to the problems of sampling a metal specimen or ingot which may not be homogeneous.

Autoradiographic techniques, on the other hand, offer the opportunity for an examination of the specimen as a whole. Radioactive materials can be located in the interior or on the surface of the ingot, or even on the walls of the container in which the metal was melted. Differences in the amounts of activity on the surface or in grain boundaries and that distributed uniformly in the major constituent are readily apparent. Segregation of the active material is easily observed.

Two types of autoradiographic examination have been used in this work: (1) macro-autoradiography, and (2) the high-resolution autoradiograph as developed by Gomberg.[3]

Specimens employed in this work were, with a few exceptions, metallic ingots obtained in the course of various studies of pyrometallurgical methods for the reprocessing of nuclear reactor fuels.

II. MACRO-AUTORADIOGRAPHY

A. Film

Several types of film were employed to accommodate the range of activities encountered. Kodak Industrial X-ray Films, Types K,* KK, AA, and M were used. Type KK is the most sensitive and has the largest grain size, with Type K next in sensitivity and grain size. Type AA is a medium-speed, medium-grain film, and Type M is a slow, fine-grain film.

B. Sample Preparation

The preparation of a metallic specimen for macro-autoradiography normally consisted of sectioning an ingot and grinding a flat face on one of the pieces. The flat side was placed in direct contact with the X-ray film. In some instances it was possible to fit the film carefully against an exterior surface of an ingot or the inside surface of a crucible when a record of activity distributions in these areas was desired. It is usually much more satisfactory, however, to use a flat cross section, if possible.

C. Exposure

The required exposure depends on the kind and amount of activity present and the type of film used. Darkening of the film results almost entirely from alpha and beta activity; gamma radiation is relatively ineffective. Since the specimens under study in this work were mostly in the form of metallic ingots, the base metals were ordinarily of high density and their good shielding characteristics limited the exposure largely to activity near or at the surface. Estimates of exposure times based on the activity of the specimen as measured with a partially shielded thin window Geiger tube eliminated the need for preliminary trial exposures in many cases. Empirical correlations for various types of film and activity were developed for this purpose. As an example of typical exposure times, satisfactory autoradiographs of bismuth, cadmium, and zinc ingots containing from 0.1 to 1.0 percent natural uranium were obtained from exposures of one to five days, using Types K and AA film.

The exposures were made in a light-tight wooden box, in which the specimen was mounted in wax. The surface of the specimen was held in close contact with the film by means of a spring-loaded, light-tight cover (see Figure 1).

D. Development

At the end of the exposure, the film was removed from the box and developed using the products** and procedures recommended by the film manufacturer.

*No longer available, this has been supplanted by Type KK film.

**Kodak Liquid X-ray Developer and Liquid X-ray Fixer.

FIGURE 1

EXPOSURE BOX FOR MACRO-AUTORADIOGRAPHY
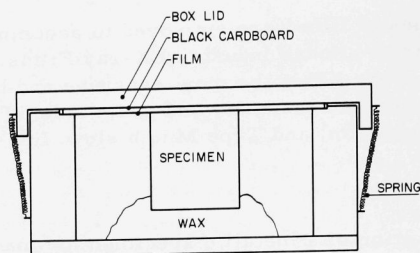
E. Interpretation

Loss of detail as a result of overexposure is one of the more common causes of misinterpretation of autoradiographs. An example of this loss in definition is shown in Figure 2. Moreover, an unexposed area on an autoradiograph is not conclusive proof that there is no activity at that position. For these reasons it is advisable to prepare at least two autoradiographs with different exposure times when a possibility for doubt concerning the proper exposure arises.

FIGURE 2

CONTACT AUTORADIOGRAPHS OF A
SOLUTION OF URANIUM IN MAGNESIUM

(A) represents a 24-hour exposure on Type AA film.
(B) is the result of a five-day exposure on the same
type of film. The loss of detail caused by over-
exposure is apparent in (B).
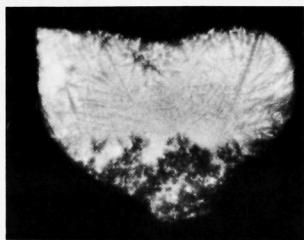
A
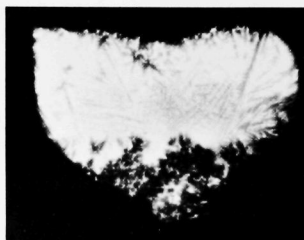
B

With uranium-containing materials practically all the activity de-
tected by instruments sensitive to beta and gamma radiation arises from
the decay products of uranium. However, photographic emulsions are
highly sensitive to alpha particles. They are less sensitive to beta radia-
tion and are scarcely affected by small amounts of gamma radiation. The
effect of alpha particles on the emulsion is about 10^3 times greater than that
of an equivalent number of beta particles, which in turn have about 10^3 times
the effect of the equivalent gamma radiation.[3]

Three uranium isotopes make up "natural" uranium, all of which
decay by alpha-particle emission. In each case, the first daughter product
is a beta-active thorium with a shorter half-life than the parent uranium
isotope. Thus the beta activity of a sample of uranium increases rapidly
after processing which removes thorium.

In each of the three decay series, an alpha-active isotope is formed
after one or two steps. In each case, the new alpha emitter has a com-
paratively long half-life, greater than 10^4 years. Thus the primary ura-
nium isotopes are the only alpha emitters significant in autoradiography of
processed uranium, and the first one or two beta-emitting daughters are
the only other significant activities to be considered. Results of a calcula-
tion showing this buildup of activity are shown in Table 1.

Table 1

GROWTH OF ALPHA AND BETA ACTIVITY IN PURIFIED URANIUM

All numbers refer to disintegrations in one gram
of uranium per second.

Calculations of decay rates.

Isotope	$T_{1/2}$	Time After Purification of Uranium					
		0		1 yr		15 yr	
		α	β	α	β	α	β
U^{238}	4.49×10^9 yr	1.23×10^4	-	1.23×10^4	-	1.23×10^4	-
Th^{234}	24.1 d	-	-	-	1.23×10^4	-	1.23×10^4
Pa^{234}	1.18m	-	-	-	5.16×10^2	-	5.16×10^2
U^{234}	2.48×10^5 yr	-	-	5.74×10^{-9}	-	5.74×10^{-9}	-
U^{235}	7.13×10^8 yr	5.77×10^2	-	5.77×10^2	-	5.77×10^2	-
Th^{231}	25.6 hr	-	-	-	5.77×10^2	-	5.77×10^2
Pa^{231}	3.43×10^4 yr	-	-	4.9×10^{-5}	-	4.9×10^{-5}	-
U^{234}	2.48×10^5 yr	1.25×10^4	-	1.25×10^4	-	1.25×10^4	-
Th^{230}	8.0×10^4 yr	-	-	0.108	-	1.65	-
Totals	2.54×10^4	2.54×10^4	0	2.54×10^4	1.34×10^4	2.54×10^4	1.34×10^4

Observed rates of alpha decay:[5]

Recently Purified Uranium 2.37×10^4 alpha/(g U)(sec)
Unpurified Mineral Uranium 9.6×10^4 alpha/(g U)(sec)

Thus, if it is assumed that alpha radiation from the uranium isotopes has about 10^3 times the effect of the beta radiation from the daughters, the proportion of the total photographic density due to the daughter products is less than 0.1 percent. Exposure of the film by penetration of alpha and beta particles from beneath the surface of the specimen has been assumed to be negligible.

Mineral uranium, with its decay products, having had several billion years to establish equilibrium, presents a different situation. The alpha particles from such material come from a number of sources, uranium isotopes contributing about one-fourth of the total number of disintegrations. [5]

F. Examples of Macro-autoradiography

The element of greatest interest in the problems which were investigated was uranium. In the first group of autoradiographs (Figures 2 through 7), uranium is shown as it was found in various solvent metals. In the second group (Figures 8 through 15), a variety of autoradiographs of other elements, for the most part fission products, is shown.

Contact prints were made from the autoradiographs presented here. Activity in the specimens is represented by the lighter areas in the prints.

Figure 3 shows the distribution of uranium in bismuth. The amount of uranium was small, about 1000 ppm. Virtually no activity could be detected with a thin window Geiger tube. The uranium is distributed throughout the ingot in the form of small particles, thereby showing that precipitation of uranium from solution had taken place during cooling. A significant portion of the activity is present at the top and bottom of the ingot.

FIGURE 3

BISMUTH CONTAINING 1000 PPM NATURAL URANIUM
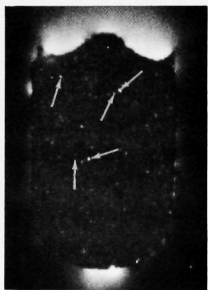
The uranium is dispersed throughout the body of the specimen in the form of small particles of a uranium-bismuth intermetallic phase which precipitated as the metal was cooled. Some of the larger particles are indicated by arrows. Exposure was 147 hours on Type K film.

In many of the autoradiographs the active metals are distributed uniformly through the specimen or are found as local deposits of particulate matter at the top, bottom, and edges of the specimen.

There are two reasons for the appearance of active metals as particulate matter. First, the active metal may be precipitated from solution as the solvent metal cools. In this case, there is usually a fairly homogeneous distribution of the activity throughout the body of the solvent metal. In the second case, an intermetallic phase or a compound may be formed either with the solvent metal or some other metal. There is ordinarily a density difference between this phase and the solvent metal so that the distribution of activity is affected. In this case, most of the activity is found either at the bottom or the top of the resulting ingot.

One other situation deserves mention. Often a contaminant such as oxygen may react with the active element. This complication can often be anticipated or recognized from the appearance of the ingot before the auto-radiograph is prepared.

Magnesium saturated with uranium is shown in the autoradiograph presented as Figure 4. In this case no intermetallic phase is formed. The active phase is pure uranium. Its solubility is low, about 10^{-2} percent, but adequate for short exposures.

FIGURE 4

MAGNESIUM-URANIUM
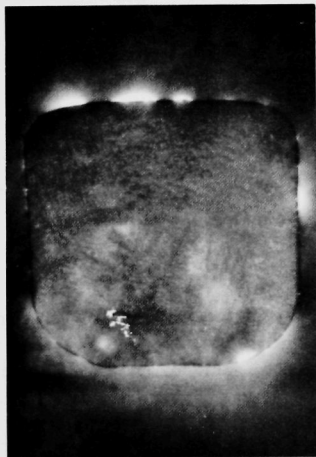
A solution of uranium in magnesium in the concentration range from 0.001 to 0.1 percent was quenched. An exposure of 24 hours on Type AA film shows the pattern in which uranium was suspended in the magnesium.

An example of reaction with a material other than the solvent metal is shown in Figure 5. A solution of uranium in cadmium was poured into a graphite crucible. After cooling, the ingot was sectioned and it appeared to be homogeneous. An autoradiograph showed the expected pattern of uranium in the body of the ingot and, in addition, a large amount of activity in the top few millimeters. Apparently some of the uranium had reacted with a third element, possibly carbon, to form a compound with a density less than that of cadmium. The intermetallic compound of uranium and cadmium has a density greater than that of cadmium.

FIGURE 5

COMPOSITE AUTORADIOGRAPH OF A LARGE
CADMIUM INGOT CONTAINING URANIUM

AREA IN WHICH
URANIUM DEPOSITED
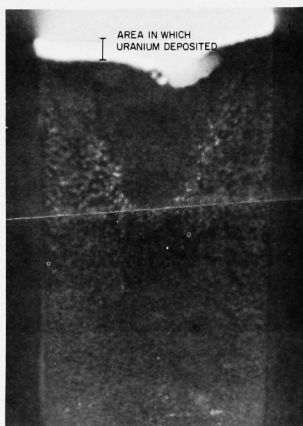
A cadmium solution of uranium was cast in a graphite crucible. Most of the uranium is present in the top of the ingot (arrow), indicating the formation of a compound which has a lower density than cadmium. In order to autoradiograph the entire ingot, it was sectioned along the vertical axis and laid across two sheets of Type AA film. The exposure was eight days.

The behavior of uranium in cadmium containing magnesium is shown in Figure 6. The uranium was almost completely precipitated. A trace of activity is to be found on top of the ingot, possibly as uranium oxide.

An autoradiograph of an ingot from the reduction of uranium oxide by a zinc-magnesium solution is shown in Figure 7. The irregular shape of the ingot results from the similarity in densities of the metal and molten salt which was used as the medium for the reaction. A layer of uranium settled to the bottom of the ingot, a region not reached by the stirring paddle. Most of the uranium within the stirred region agglomerated into a single lump.

FIGURE 6

URANIUM-CADMIUM INTERMETALLIC COMPOUND PRECIPITATED
FROM A CADMIUM-MAGNESIUM SOLUTION

Cd-Mg
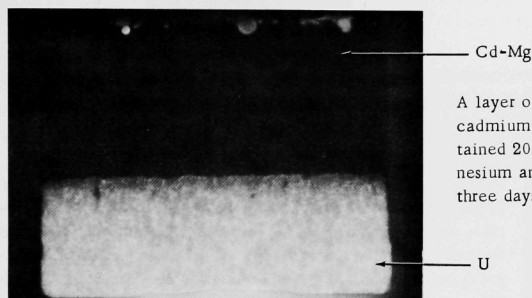
A layer of uranium is shown as it settled from a cadmium-magnesium solution. The ingot contained 200 grams each of cadmium and magnesium and 35 grams of uranium. Exposure was three days on Type AA film.

U

FIGURE 7

REDUCTION OF URANIUM OXIDE BY A
ZINC-MAGNESIUM SOLUTION

Mg-U

A molten salt flux containing 50 grams of U_3O_8 was contacted with a liquid metal phase containing approximately 200 grams each of zinc and magnesium. The uranium oxide was reduced to the metal, which settled to the bottom, except for a portion which was formed into a ball by the stirrer. The irregular shape of the final ingot resulted from the similar densities of the salt and metal phases. Exposure was three days on Type AA film.

U
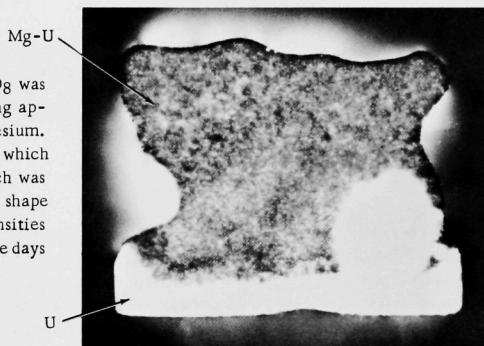
About 1000 ppm of lightly irradiated uranium was dissolved in bismuth in a mild steel container. After dissolution, the container and the bismuth were sectioned through the long axis for autoradiography. As shown in Figure 8, most of the active fission products were found deposited on the walls and bottom of the bismuth ingot. The material remaining in the bismuth was deposited in streaks resembling grain boundaries.

One of the important fission products of uranium is ruthenium. It is a noble metal, and it would be expected to behave differently than uranium and fission products higher in the electromotive series. As can be seen from Figure 9, dissolution in bismuth produced a homogeneous ingot except for a few spots of higher activity along the sides.

FIGURE 8

BISMUTH CONTAINING APPROXIMATELY
1000 PPM IRRADIATED URANIUM

Top of
Crucible

Edge of
Crucible
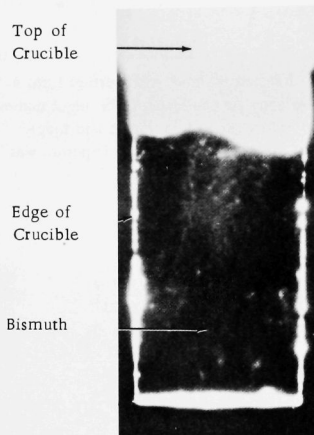
Bismuth

Mildly irradiated uranium was dissolved in liquid bismuth. The mild steel crucible containing the resulting ingot was sliced vertically and left in position around the ingot. The activity at the top and at the interface between the bismuth and the crucible shows that much of the active material was not dissolved by the bismuth. Most of the activity within the body of the ingot is present as streaks resembling grain boundaries in bismuth. The activity of the specimen ranged from 2 mr/hr in the body to 20 mr/hr at the top surface. Exposure was 6 hours on Type K film.

FIGURE 9

IRRADIATED RUTHENIUM IN BISMUTH

An autoradiograph of a cross section of a ruthenium-bismuth ingot indicates the nearly homogeneous distribution of ruthenium. Undissolved spots of high activity on the sides of the specimen exposed the film in a "halo" around a portion of the circumference. Approximately 1000 ppm of ruthenium in the bismuth produced this autoradiograph in a one-hour exposure on Type K film.
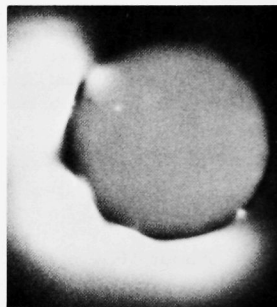
A sample of the bismuth solution of ruthenium was rocked with zinc in a stainless steel (Type 446) capsule at 500 C for 24 hours. The zinc, which is immiscible with bismuth and is of lower density, extracted the ruthenium from the bismuth almost quantitatively. In Figure 10, a trace of activity can be seen at the steel-bismuth interface as a result of the wetting of the steel by zinc. Since bismuth expands on cooling and also freezes at a lower temperature than zinc, part of the bismuth flowed over the top of the zinc.

FIGURE 10

EXTRACTION OF RUTHENIUM FROM BISMUTH BY ZINC

Zn Phase
with Ru *

Zn Layer
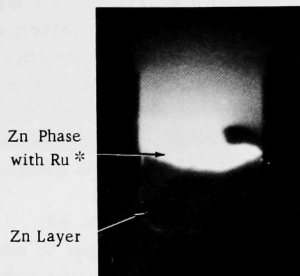
Ruthenium was removed from a bismuth solution by extraction into liquid zinc at 500 C. The dark bismuth phase, the light, lens-shaped zinc phase containing the ruthenium, and a thin line around the interior surface of the capsule where it was wet by the zinc phase are apparent. Exposure was one hour on Type K film.

An autoradiograph of cerium in bismuth is shown in Figure 11. Unlike ruthenium, which is soluble in bismuth, cerium forms an intermetallic compound with bismuth which is insoluble at temperatures near the freezing point. The intermetallic compound is slightly less dense than bismuth. An even dispersion of the intermetallic compound was achieved in this ingot by rapid quenching.

FIGURE 11

DISPERSION OF CERIUM IN BISMUTH
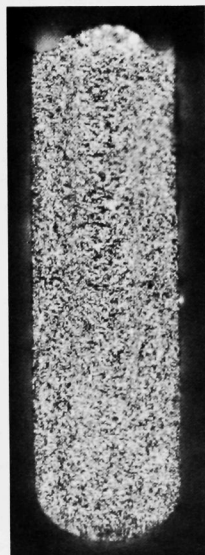
An even dispersion of cerium in bismuth was achieved by agitation and quenching of the ingot just above the freezing point. Approximately 2000 ppm of irradiated cerium were used. Exposure was 40 minutes on Type K film.

Distribution of cerium in bismuth as a function of the heating and cooling treatment is shown in Figure 12. In each case, the exposure of the autoradiograph was one hour on Type K film; the only variables are the heat treatments and cooling rates. Portions of a single large ingot were used for the treatments. After the bismuth solution was held molten at 600 C for one hour and quenched in air, the activity was found largely in the top few millimeters of the ingot. The particles of intermetallic were very small. This is shown in Figure 12A. Figure 12B shows the larger particles of intermetallic obtained by cooling the molten bismuth from 600 C at a slow rate, about 1 degree C per minute.

FIGURE 12

EFFECT OF HEATING AND COOLING TREATMENT
ON THE DISTRIBUTION OF CERIUM IN BISMUTH

Several autoradiographs were used to examine the distribution of cerium in bismuth as a function of heat treatment. Portions of a single larger ingot were used for the individual treatments. Each exposure was one hour on Type K film. The treatments were as follows:

(A) Held for one hour at 600 C, quenched by air.
(B) Cooled slowly (1 degree C/min) from 600 C.
(C) Cooled from 600 to 400 C, then quenched by water.
(D) Cooled from 600 to 300 C, then quenched by air.
(E) Held for 16 hours at 600 C, quenched by water.

A   B   C

D   E
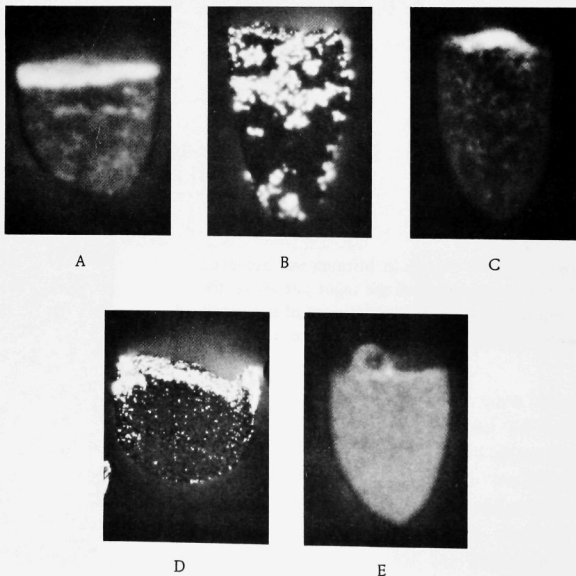
In another experiment, the metals were held at 600 C for one hour and at 400 C for one hour then quenched in water; Figure 12C shows that the activity is now largely in the body of the bismuth, with much of it present as large intermetallic crystals. Larger intermetallic particles were obtained when the materials were held at 600 C for one hour, followed by holding at 300 C for one hour, then air quenching. Figure 12D shows the larger intermetallic particles that were formed by this procedure. An almost perfectly homogeneous dispersion of the cerium was achieved, as shown in Figure 12E, by holding the mixture at 600 C for 16 hours, then quenching it in water.

An attempt was made to extract cerium from bismuth with zinc by means of the same method used to extract ruthenium. In this case, the cerium remained in the bismuth phase as is shown in Figure 13. The zinc phase is not visible in this autoradiograph.

FIGURE 13

ATTEMPTED EXTRACTION OF CERIUM FROM BISMUTH WITH ZINC

Results of an attempt to extract cerium from bismuth with zinc are shown in this autoradiograph. The radioactive cerium can be seen as light spots in the bismuth phase; the zinc phase contained no activity and thus is not visible. One hour exposure on Type K film.

It is possible to obtain good autoradiographs of highly active materials in some cases. An ingot of cadmium containing activated lanthanum which had an activity of nearly 200 mr/hr was prepared. Type KK or Type AA films yielded unsatisfactory autoradiographs because of overexposure in times as short as ten minutes. Figure 14 shows the results of a 30-minute exposure of the ingot on Type M film. Nearly all the activity can be seen on the bottom of the ingot as a lanthanum-cadmium intermetallic phase, with traces at the top surface which probably resulted from oxide contamination.

Occasionally an autoradiograph is obtained which has the appearance of a photograph of the specimen. One of these is shown in Figure 15. A strip of mild steel was exposed to 200-psi steam from water which had passed over a small piece of irradiated uranium. The three sections of the autoradiograph represent a single long piece of metal. Features at the bottom of section (c), the lower end of the strip, were caused by the

clamping device. The deposition of activity seems to be associated with the visible effects of corrosion. Edges of corrosion pits are outlined particularly well. Information of this type would be difficult to obtain by a method other than autoradiography.

FIGURE 14

CADMIUM INGOT CONTAINING ACTIVATED LANTHANUM

Cd

La*-Cd
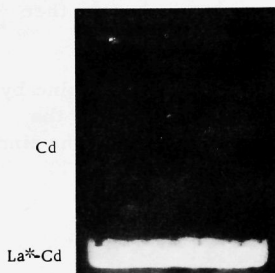
The formation of a lanthanum-cadmium intermetallic compound of higher density than the cadmium resulted in the layer at the bottom of the ingot. The traces of activity on the surface probably represent small amounts of lanthanum oxide. The activity of the section, about 200 mr/hr, was too high for Types K or AA film. Type M film, however, gave a satisfactory image after a 30-minute exposure.

FIGURE 15

DEPOSITION OF FISSION PRODUCTS ON MILD STEEL

Steam which had been in contact with irradiated uranium was passed over mild steel to study the deposition of fission products. The three sections are from a single long specimen of the mild steel. Type AA film was used.
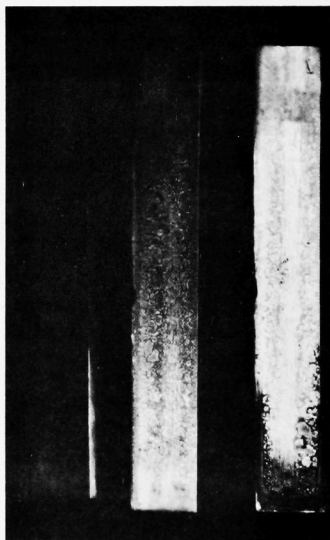
III. HIGH-RESOLUTION AUTORADIOGRAPHY

The high-resolution autoradiograph represents one of the most sensitive methods for detecting radioactivity. Individual disintegrations can be detected and the precise location of the disintegration can be determined. Several methods for producing high-resolution autoradiographs have been developed, for the most part in connection with biological studies.[4] To a lesser extent, work has also been done with geological and metallurgical[3] specimens.

A. Film

Much of the early high-resolution work was done with liquid emulsions prepared in situ.[6,7] More recently, nuclear emulsions have become available in pellicles or in bulk form. Among these are the Kodak NTA[8] and NTB[9] emulsions and the VEB Agfa Wolfen liquid K-2 emulsion.[10]

There are now available several types of thin emulsions with high silver density, which are suitable for autoradiography of metallurgical specimens. The ones used in this work were the Kodak Experimental Permeable Base Autoradiographic Stripping Film and the Kodak Autoradiographic AR-10 Stripping Plates, made in England.

Stripping films differ from other film in that the emulsion is supported, not on a plastic, but on a water-permeable gelatin film. Thus the emulsion can be placed on the specimen, exposed, developed, and examined in situ. As the autoradiograph is examined, tracks in the film can be correlated directly with the appearance of the specimen.

The permeable base stripping film is supplied in 35-mm rolls on a plastic-backing film. The emulsion and supporting gelatin film are each five microns thick and are stripped together from the plastic before use. The AR-10 stripping plates provide a ten-micron-thick emulsion with a gelatin support on a glass slide. It is used in the same manner as the permeable base stripping film, but it is considerably more substantial. The thinner film has little strength when wet and thus requires delicate handling.

B. Sample Preparation

It has proved convenient to prepare specimens for autoradiography much as they are prepared for metallurgical examination. The specimens were normally less than two centimeters in any one dimension. They were mounted in Bakelite for convenience in handling. Smaller or more delicate samples were frequently mounted on microscope slides, while occasional larger ones were not mounted at all.

The metal specimens were ground on a metallurgical polishing wheel down to a 600 grit abrasive to provide a smooth surface for the stripping film. They were then etched with a suitable solution, depending on the base metal. In some types of specimens etching was not required, or even advisable. In these samples there was a tendency for dust, including radioactive particles produced in grinding and polishing, to deposit in cracks, surface imperfections, edges of the specimen, or elsewhere. Such deposits will, of course, cause trouble in the interpretation of the resulting autoradiograph. However, several layers of collodion solution painted over the surface of the specimen were found to form a thick coating which could be peeled off, thereby removing most of the fine particles.

It was then necessary to apply a thin permanent coating to the surface of the metal specimen for the purpose of (1) preventing reduction of the silver halide in the emulsion by reactive metals in the specimen, and (2) preventing reaction of the metal with the developing solutions. A Vinylite VYNS (90 percent vinyl chloride, 10 percent vinyl acetate) solution in methyl ethyl ketone provided the necessary protection with a minimum film thickness. If the specimen is dipped into a two percent solution and dried under a heat lamp for about 30 minutes, the film is approximately one micron thick.[7]

The gelatin emulsion often tended to peel off the specimen either during exposure or on processing. It proved beneficial to dry a few drops of gelatin solution on the surface of the specimen prior to placing the film. For this purpose a one-half percent solution of dry gelatin in water containing 1/2000 Zephiran chloride germicide and wetting agent was used.

C. Application of Emulsion

Two methods were used to apply the emulsion to the specimen. The simpler and generally more satisfactory technique consisted of stripping the film and floating it on the surface of two or three inches of water in a tray. After the film had been soaked for about two minutes, the specimen was brought up through the water at an angle. The film first touched the specimen at one edge, and as the specimen was pulled out of the water the film adhered to it. When the specimen was held at an angle, the excess water flowed to one side and was removed by touching the edge with an absorbent tissue.

In the second method, the tray of water was not used. Instead, the film was floated on a few drops of water or gelatin solution placed directly on the specimen. When the film had absorbed sufficient water, the excess was removed in the same manner as before, leaving the film on the specimen. With either of these techniques care was necessary to avoid foreign material on the surface of the water.

The dry film as supplied on the plastic or glass mount is of the nominal five- or ten-micron thickness. As it absorbs water, it swells in thickness and increases in area to about one and one-half times its original dimensions. When the film is dried on the specimen the emulsion is spread over a larger area and is therefore thinner. Also, it is under some tension and is quite susceptible to peeling or tearing.

Application of the film by either method must, of course, be done in a dim red light. A standard red photographic "safe light" at a distance of about four feet was found satisfactory.

After the film was mounted on the specimen, it was allowed to dry for a few minutes, then placed in a light-tight box. The box was placed in a refrigerator at 5 C for the duration of the exposure to decrease the possibility of chemical reaction between the film and the specimen materials. A desiccant such as calcium chloride may be placed in the box to maintain a constant, low humidity.

D. Exposure

The time of exposure depends on the type and amount of activity present and the sensitivity of the film. Since the base metals used in this work were dense, the self-shielding was sufficient so that virtually all the tracks appearing in the autoradiographs resulted from activity present at the exposed surfaces of the specimens. Films on pure natural uranium phases were almost completely covered with alpha tracks in five days, whereas films over phases dilute in uranium, such as the intermetallic phase UCd_{11}, showed 10 to 50 alpha tracks over crystals of 0.005 to 0.01 sq mm in area.

E. Development

The films were developed in Kodak D-19 for five minutes at 20 C. The solutions were applied directly to the emulsions by means of medicine droppers. A normal or fast fixing solution was applied for a time sufficient to clear the emulsion. The film was then washed by gently dropping water on one edge and allowing it to flow across the surface. Washing must be done carefully to avoid disturbing the placement of the film. Because the emulsion is thin, however, only two or three minutes of washing are necessary.

All the developing operations were performed under the illumination of a red "safe light."

F. Examination

When the high-resolution autoradiograph was dry, it was examined with a metallurgical microscope. Since the film was still adhering to the specimen, the activity tracks could be correlated directly with visual observations of features on the surface of the metal.

High magnifications were not required for inspection of the films, nor were they particularly desirable in many instances. Using objectives of 20 to 25X, alpha tracks were readily visible, and the depth of field was sufficient so that the tracks in the film and the surface of the specimen could both be maintained in reasonably sharp focus at the same time.

At this magnification the tracks were sometimes rather small, making them difficult to distinguish from the darker areas in the speci- men. Under these circumstances, higher magnifications were used. Objectives of 40 to 63X proved satisfactory. The specimen was left out of focus while the activity tracks were located and then, by changing focus, the surface of the specimen was examined.

G. Preservation

When it was desired to preserve a high-resolution autoradiograph, it was found advisable to remove the film from the specimen and mount it on a microscope slide with a cover glass, much as histological speci- mens are prepared. Not only did this help to preserve the film, but in this condition it was generally found that more tracks were visible when the film was viewed by transmitted light. Ordinarily, there was sufficient replication of the specimen surface so that the tracks could be correlated with the surface structure.

While mounting of the film is usually desirable, it can be a diffi- cult operation with the permeable base stripping film. When dry, the film adheres tightly to the specimen, and it will probably be torn if removal is attempted. When wet, it has little strength. Application of water containing a wetting agent softens the emulsion. It can then be separated from the specimen by starting at one edge, lifting it with a dissecting needle, and folding this portion back over the rest of the film. When the entire film is loose, it can be lifted on a micro-spatula or with flat forceps and placed on the glass slide in a few drops of water. Using the dissecting needle and small forceps, the film can then be straightened and unfolded. After thorough drying in air, a cover glass can be fixed in place with a mounting cement such as "Permount."*

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*Fisher Scientific Company

H. Photography of Autoradiographs

Photographic reproductions of autoradiographs are frequently desired as permanent records. A variety of devices is available for adapting microscopes to photographic purposes. The major factor in selecting such equipment is in the choice of film size. Although adapters can be furnished for film sizes from 8 mm to 5 x 7-in. plates, four types are in common use. These consist of 35 mm, $3\frac{1}{4}$ x $4\frac{1}{4}$-in. glass plates, 4 x 5-in. or 5 x 7-in. sheet film and "Polaroid" films. Each has its advantages and disadvantages; the final choice must be left to individual preferences and requirements.

Because of its economy and versatility, 35-mm equipment is most widely used. By the use of the newer thin-emulsion, fine-grain films, such as Kodak Panatomic X and Adox KB-14, photomicrographs of good contrast can be obtained which are suitable for considerable enlargement if desired. Also, inexpensive color films can be used with no changes in accessories. Most of the photomicrographs reproduced here were taken with 35-mm equipment.

For quick photomicrographic positive prints, for limited use such as a research notebook, the Polaroid attachments are most useful. Exposures can be progressively adjusted to obtain high-quality pictures.

Large sizes of sheet film are probably the most generally useful and certainly the most versatile. Contact prints which are generally superior to enlargements, can be made for reproduction purposes. Also, a larger variety of emulsions is available, including color types, in sheet film.

The photomicrographs of highest quality have almost invariably been obtained with glass plates. These are dimensionally stable, optically flat at all times, and are available in emulsions particularly suited to the problems of photomicrography. Glass plates are expensive and fragile; however, excellent reproductions are made possible through their use.

Further discussion of the films and techniques can be found in the extensive literature devoted to photomicrography.[11]

At high magnifications, photographic representation of high-resolution autoradiographs is difficult. The limited depth of field of the microscope objective prevents simultaneous focusing of particle tracks in the emulsion and the surface of the specimen. In fact, the track of a particle is often only partially visible, because it passes through the emulsion at an angle. During visual observation of the tracks, the focus can be changed continuously to correlate a track with its origin at the

surface of the specimen. While photomicrographs at such high magnification are seldom necessary to illustrate the phenomenon being studied, two photographs can be taken, one at a plane of focus in the emulsion and a second at the specimen surface for comparison. These problems generally arise when objectives of greater than 40X are used.

I. Examples of High-resolution Autoradiography

Photomicrographs of several autoradiographs are presented here as examples of the sort of information one can gain from this technique. A few of the examples are treated in some detail with regard to experimental conditions and include several illustrations because of the difficulty in presenting a single meaningful photomicrograph of an autoradiograph. Unfortunately, it is difficult to secure a high-magnification photomicrograph having the depth of field one obtains by illusion as the plane of focus is moved up from the surface of the specimen through the film.

A single crystal of the intermetallic phase UCd_{11} is shown in Figure 16. In an area of about 0.002 sq mm it contains about 50 alpha tracks and several beta tracks. The specimen was prepared by polishing and etching a cadmium-uranium ingot as for metallurgical examination. The chromic oxide etching solution preferentially dissolved the cadmium, leaving the intermetallic crystals protruding slightly from the surface. This stretched the film tightly over the crystal. The focus is in the plane of the emulsion, the surface of the intermetallic phase is slightly out of focus, and the cadmium surface and the film over this portion are completely out of focus.

In the upper right-hand corner of the crystal, a dark area indicates that there may have been a small break in the protective film which allowed some reaction to take place between the metal and silver halide in the emulsion.

Autoradiography is perhaps the simplest method for detecting weak beta-emitting isotopes, such as nickel-63, which is almost undetectable with most counting equipment. A film of nickel-63, 7000 Angstroms thick, was plated on a coupon of high-purity, vacuum-melted nickel. The coupon was then heated for four days in an oxygen atmosphere at 960 C.

Kodak AR-10 Autoradiographic Stripping Film was exposed for five days to obtain the autoradiograph shown in Figure 17. The distribution of active nickel through a major portion of the oxide layer indicates a reaction mechanism involving the diffusion of nickel through the previously formed layer of nickel oxide.[12]

FIGURE 16

## ALPHA AND BETA TRACKS PRODUCED BY CRYSTAL OF URANIUM-CADMIUM INTERMETALLIC COMPOUND

A crystal of UCd_{11} was used to prepare an autoradiograph. Both alpha and beta tracks are present and are indicated by arrows. A Zeiss metallurgical microscope with a 63X objective and a 35-mm camera attachment was used. The total magnification is approximately 1600X. The small dark spot on the upper right corner of the specimen was caused by reaction of the metal with the silver halide in the emulsion.
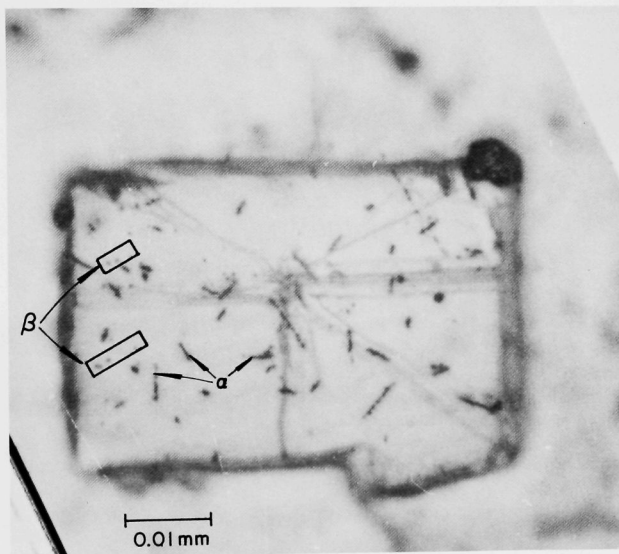
A coupon similarly plated was treated with fluorine. The film of nickel fluoride was not adherent but was separated and mounted in a dental plastic. It was polished normal to the plane of the coupon surface. The autoradiograph is shown as Figure 18. All the active nickel was found in a narrow band on the outside of the specimen. There was no diffusion of active nickel through the film as in the case of the oxygen reaction. This indicates a different mechanism involving diffusion of fluorine through the film to the surface of the nickel.

Magnification of these autoradiographs by a factor of 100 is in marked contrast to that shown in the previous figure. In this case the individual beta tracks in the film are not resolved, only the darkening of the film in the areas of activity is visible.

FIGURE 17

OXIDATION OF A NICKEL SURFACE
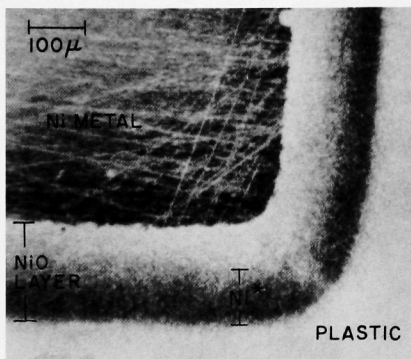
A nickel specimens was plated lightly with radioactive nickel-63 and exposed to oxygen at 960 C. An auto-radiograph of a section of the specimen was then prepared. The diffuse nature of the darkened area indicates that the radioactive nickel has migrated within the nickel oxide layer. A Leitz Panphot with a 3.5X objective was used to give 100X magnification on the 4 x 5-inch Kodak Super X film.

FIGURE 18

FLUORINATION OF A NICKEL SURFACE

Radioactive nickel-63 was plated on a nickel specimen which was then exposed to gaseous fluorine at elevated temperatures. The autoradiograph shows the active nickel in a narrow band along the outside surface of the nickel fluoride layer. This indicates little if any diffusion of nickel in contrast with the nickel-oxygen reaction indicated in Figure 17. In this case, the nickel fluoride layer was separated from the nickel specimen and mounted in dental plastic. The photomicrograph was prepared in the same manner as the one for Figure 17.
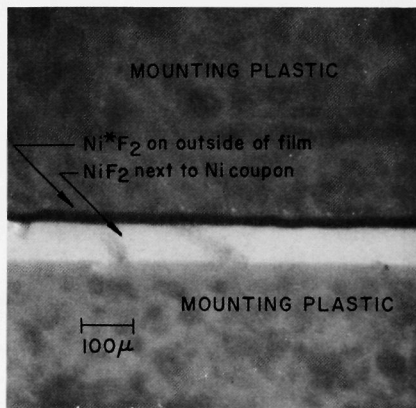

A nickel coupon was suspended in molten cadmium which also contained uranium. The system was maintained at 560 C for 24 hours without stirring, then slowly cooled. The resulting ingot was cut vertically through the coupon, polished, and etched. A low-magnification photomicrograph (Figure 19) shows the tip of the dissolving nickel coupon. In the immediate area of the coupon are small particles of nickel breaking away from the main body.

FIGURE 19

DISSOLUTION OF NICKEL BY A
CADMIUM-URANIUM SOLUTION:
200X MAGNIFICATION

A nickel specimen was exposed to a solution of uranium in molten cadmium at 560 C. The ingot containing the undissolved nickel was sectioned and autoradiographed. The photomicrograph was taken at low magnification (100X) with a Zeiss metallurgical microscope and a 35-mm photo attachment.
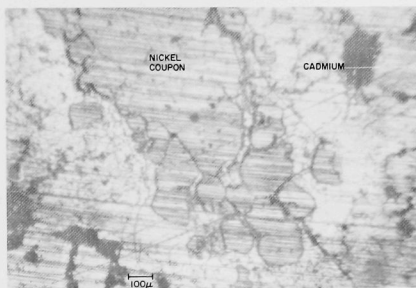
Alpha tracks indicating the presence of uranium appear in large numbers along the edges of the nickel fragments. These tracks seem to be associated with a phase which is most likely a nickel-uranium intermetallic compound, insoluble in cadmium. Figures 20 and 21 represent the same area, the first with the plane of focus at the metal surface, showing the dissolving edge of a nickel fragment. The second is focused on the alpha tracks in the film just above the metal surface.

Two types of experiments demonstrated the formation of an iron-uranium intermetallic phase which is also insoluble in cadmium. Cadmium solutions of uranium, when contained in iron or steel, were found to lose uranium over a period of time. The loss of uranium became particularly significant at temperatures above 750 C.

A bundle of iron wires was placed in a cadmium-uranium solution and held at 700 C for several hours. After cooling, the ingot was cut, exposing sections of the iron wires. It was polished and lightly etched with a chromic oxide solution which dissolved the surface layers of cadmium but did not attack the iron.

FIGURE 20

DISSOLUTION OF NICKEL BY A CADMIUM-URANIUM SOLUTION: 1600X MAGNIFICATION

A high-magnification photomicrograph (1600X) of the specimen shown in Figure 19 was prepared. The microscope was focused on the plane of the metal surface. Few of the alpha and beta tracks are visible except in the low area between the two nickel-rich fragments, where some cadmium was removed by the etching solution. A Leitz Panphot microscope was used with a carbon arc and Kodak Metallurgical glass plates.
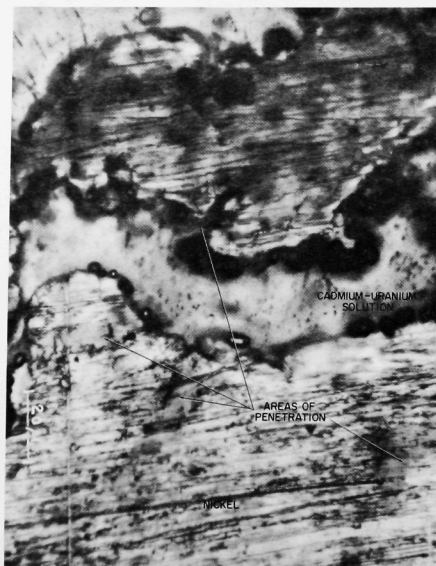

FIGURE 21

DISSOLUTION OF NICKEL BY A CADMIUM-URANIUM SOLUTION: ALPHA AND BETA TRACKS

A photomicrograph of the same area shown in Figure 20 was taken with the microscope focused on the plane of the autoradiographic film. Alpha and beta tracks are much more readily visible than in Figure 20. The nickel fragment at the top of the illustration shows considerably more reaction with uranium than the lower one. It is nearly covered with alpha and beta tracks. Alpha tracks can be correlated with the dark, partially dissolved, areas in the nickel-rich phase. A few of the beta tracks are circled. The same equipment was used as for Figure 20.

A high-resolution autoradiograph of the specimen revealed each of the iron wires to be surrounded by an alpha-active material, presumably an iron-uranium intermetallic. Two such iron wires are shown in Figure 22. The surface of the iron wire has been attacked and alpha tracks are located well within this layer. When the emulsion was lifted from the specimen, a photomicrograph, shown in Figure 23, was obtained. The alpha tracks at the iron-cadmium interface are more easily distinguished.

FIGURE 22

IRON WIRES EXPOSED TO A
CADMIUM-URANIUM
SOLUTION

Iron wires were exposed to a cadmium-uranium solution at 700 C. The ingot was sectioned to expose the wires. The photomicrograph shows two of the wires penetrated by the solution to depths up to 0.02 mm. A band of alpha tracks, several of which are indicated by arrows, can be distinguished in this region, suggesting the formation of an iron-uranium intermetallic compound. Large black spots along the edges of the wires are caused by reaction of the metal with the silver halide in the emulsion. The photomicrograph, taken with a Zeiss metallurgical microscope and a 35-mm attachment, is enlarged to about 375X.
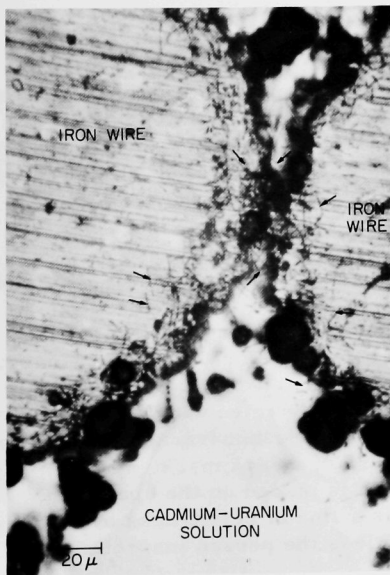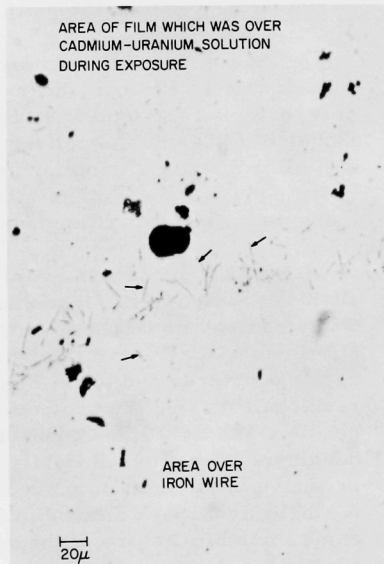
FIGURE 23

EXAMINATION OF AUTO-
RADIOGRAPHIC EMULSION
BY TRANSMITTED LIGHT

An autoradiographic emulsion was lifted from the specimen and examined by transmitted light at about 250X magnification. The specimen was an iron wire in cadmium-uranium similar to that shown in Figure 22. Again a few of the alpha tracks are indicated by arrows. The black areas are similar to those noted in Figure 22. A standard Leitz microscope was used with a 35-mm camera attachment.

IRON WIRE

IRON WIRE

CADMIUM-URANIUM
SOLUTION

20μ

AREA OF FILM WHICH WAS OVER
CADMIUM-URANIUM SOLUTION
DURING EXPOSURE

AREA OVER
IRON WIRE

20μ

An autoradiograph of one of these iron wires, which was cut nearly parallel to its axis, is shown in Figure 24. The density of alpha tracks within the surface layers of iron is shown.

FIGURE 24

EXAMINATION OF ALPHA TRACKS BY TRANSMITTED LIGHT

In this photomicrograph the emulsion was again lifted from the specimen and examined by transmitted light. An iron wire in the cadmium-uranium ingot was sectioned in a plane nearly parallel to its axis and just within the reacted layer. The protective film in this autoradiograph was also penetrated in several small areas, permitting reduction of the silver halide by the metal specimen and producing the black spots on the film. The equipment and magnification used were the same as for Figure 23.

In a different type of experiment, a cadmium-uranium solution was circulated for many hours in a mild-steel loop. A small cross section of a portion of the loop was taken after freezing the cadmium. It was mounted in plastic and polished. An autoradiograph of this section showed a similar affinity of iron for uranium. There were few alpha tracks found in the body of the cadmium. At the iron-cadmium interface, however, there was a significant amount of activity, as is shown in Figure 25.

It is important to avoid misinterpretation of marks in the emulsion such as are shown in Figure 26. The emulsions are pressure sensitive. Thus manipulations during cutting, handling, and placing the film on the specimen will all leave their mark. Since the films are fragile, they are easily punctured and torn. Some of the black areas on the figure are a result of breaking the protective layer on the specimen with a dissecting needle. The light lines connecting the tears represent tracks of the same needle as it was moved lightly over the surface. Such marks may be produced in attempts to move the film as it is placed on the specimen. A single light mark may be interpreted as a line of beta tracks overlaying some invisible feature of the specimen unless the person inspecting the film is aware of this possibility.

FIGURE 25

AUTORADIOGRAPH OF A STEEL CORROSION
TEST LOOP SECTION

An autoradiograph was prepared of a section taken from a steel tube used as a corrosion test loop for cadmium-uranium solution. A significant accumulation of alpha tracks along the interface between the cadmium solution and the steel indicates the precipitation of uranium, probably as an iron-uranium intermetallic compound. As in Figures 23 and 24, the emulsion was removed from the specimen for this photomicrograph. An American Optical microscope with 35-mm camera equipment was used. The enlargement is about 500X.
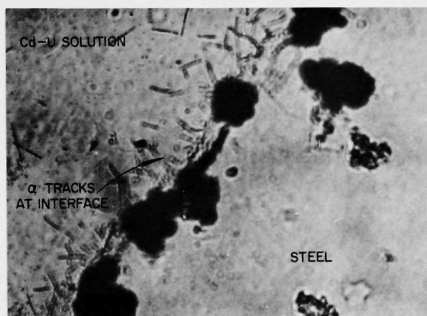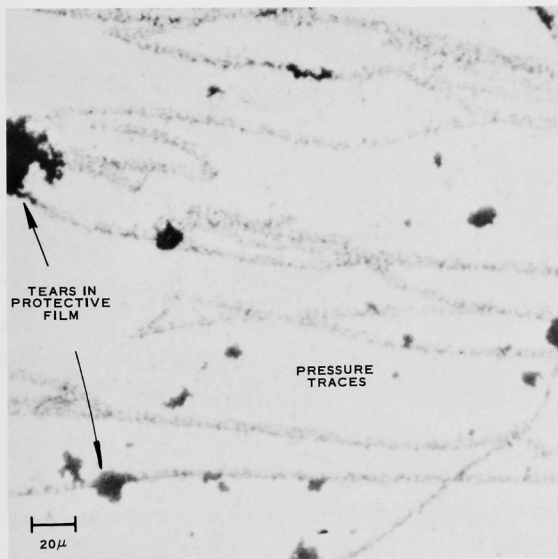

FIGURE 26

EFFECTS OF MISHANDLING AUTORADIOGRAPHIC EMULSIONS

Mishandling of an autoradiographic emulsion can produce effects subject to misinterpretation. The scratches and tears shown in this photomicrograph were produced by a dissecting needle. The light streaks were caused by pulling the needle gently across the pressure sensitive emulsion. The darker areas resulted from breaking the protective layer on the metal specimen, allowing it to reduce the silver halide in the emulsion. A standard Leitz microscope with 35-mm camera equipment was used to photograph the emulsion after it was removed from the specimen. The magnification is about 400X.

IV. CONCLUSIONS

Autoradiographic techniques can be used effectively under many circumstances to supplement information on metallic specimens obtained by metallographic and chemical analysis. In most instances, a sample prepared for metallographic examination can be used directly for autoradiography, which is a nondestructive technique. Autoradiographic observations are of particular value in examining the behavior of trace quantities of materials which cannot be detected by metallographic methods.

ACKNOWLEDGEMENTS

REFERENCES

1. H. Becquerel, Compt. rend. 122, 501, 689 (1896).

2. A. N. Davenport and G. W. W. Stevens, Nature, 174, 178-9 (1954).

3. H. J. Gomberg et al., Final Report, High-Resolution Autoradiography for Study of Grain Boundaries in Metals, WAL-843/13-19-2029-J-F (Feb. 1954).

4. W. P. Norris and L. A. Woodruff, Ann. Rev. Nucl. Sci. 5, 297 (1955).

5. H. Geiger and E. Rutherford, Phil. Mag., (6), 20, 691-8 (1910).

6. A. J. Oliver, Laboratory Production of Fine Grain Nuclear Emulsion, UCRL-5273-T (July 1958).

7. G. C. Towe, H. J. Gomberg, and J. W. Freeman, High Resolution Autoradiography, NACA-1243 (1955).

8. J. A. Builbert and J. A. S. Adams, Nucleonics 13, 43 (July 1955).

9. T. K. Bierlein and B. Mastel, Rev. Sci. Inst. 30, 46 (1959).

10. W. Malz, Kernenergie 1, 813 (1958).

11. R. M. Allen, Photomicrography, D. Van Nostrand Co., Inc, New York (1958).

12. Chemical Engineering Division Summary Report for July, August, September 1960, ANL-6231, p. 104.